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Polybrominated Diphenyl Ethers Contamination in Marine Organisms of Yantai Coast, Northern Yellow Sea of China

Jing Chen · Linlin Chen · Dongyan Liu · Gaosheng Zhang

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Abstract To evaluate the contamination of polybrominated diphenyl ethers (PBDEs) in marine organisms of the northern Yellow Sea of China, mollusks, wild shrimps and crabs were collected from the Yantai coast and ten PBDE congeners levels in the samples were analyzed and compared. The results indicate all the samples have been contaminated by PBDEs and PBDEs concentrations varied in individual species and in sampling sites. The concentration range of $\sum$PBDEs in the samples was 0.23–10.56 ng/g d.w. below the national edible criteria 40 ng/g d.w.. Congener compositions were mainly dominated by BDE 209.

Keywords Northern Yellow Sea · Polybrominated diphenyl ethers · Pollution monitoring · Seafood

Polybrominated diphenyl ethers (PBDEs) are a group of brominated flame retardants (BFRs) widely used in plastics, textiles, electronics and other materials, and have attracted widespread scientific and regulatory attention. PBDEs have some physicochemical properties similar to other persistent organic pollutants (POPs), which are known to bioaccumulate in the environment (de Bruyn et al. 2009; Hites 2004). Concentration of PBDEs in biota is estimated to have been doubling every 5 years and was reported to have increased by 60-fold in human breast milk in Sweden between 1972 and 1997 (Meironyte et al. 1999). PBDE's have been shown to be increasing more slowly in Europe and North America following the withdrawl of penta- and octa-BDEs' use and production (Pan et al. 2011). In China however, both production and consumption of BFRs including some PBDE products have risen rapidly in recent years. Marine organisms can accumulate contaminants from their environment and food chain and some of them can be used to indicate the pollutant levels. Therefore, it is important to evaluate PBDEs content and monitor their accumulation in the marine environment and organisms for seafood safety and the health of consumers.

Sishili Bay (SB) is an important shallow cultivation area in northern Yellow Sea, China, which is subject to the intense human activity from the surrounded city of Yantai. Over the last decades, the rapid industrialization, urbanization and population development in Yantai city have stressed the surrounding coastal ecosystems. POPs released from the intensive agricultural and industrial activities have been regarded as one of the pollutant sources impacting the health of marine coastal environment and organisms (Fung et al. 2004). Previous studies have showed that the increased POPs along the Yantai coast could cause potential risk for the seafood (Liu et al. 2008; Leng et al. 2009). It is essential to evaluate the PBDEs contents in the marine organisms along the Yantai coast for seafood safety. In this study, mollusks, wild shrimps and crabs were collected from a local seafood market and from the field in the SB, respectively. The PBDEs concentration in wild and aquacultured organisms were studied and compared, aiming to monitor the seafood safety and assess the potential risk to human health.

Materials and Methods

For comparing with the different marine environments, sampling areas were designed in the sewage outfall area,

J. Chen · L. Chen · D. Liu · G. Zhang (✉)
Key Laboratory of Coastal Zone Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research (YIC), Chinese Academy of Sciences (CAS), Shandong Provincial Key Laboratory of Coastal Zone Environmental Processes, YICCAS, Yantai, Shandong 264003, People's Republic of China
e-mail: gszhang@yic.ac.cn

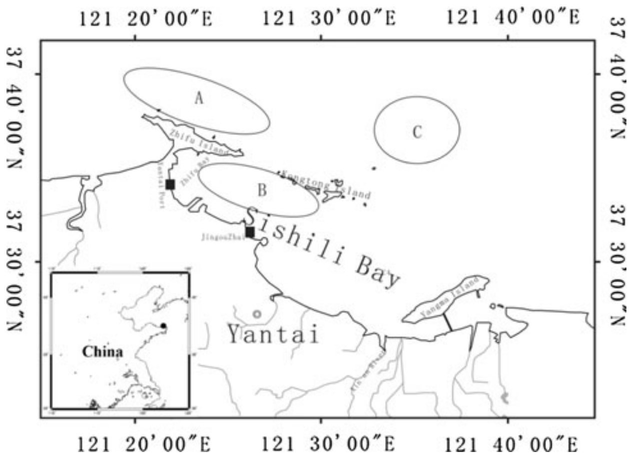

Fig. 1 The sampling sites in Yantai Sishili bay for collecting wild marine organisms (Site *A*: sewage outfall area; Site *B*: port area; Site *C*: contrast area)

Yantai port area and less human activity area as the contrast area (Fig. 1). Two species of shrimps and one species of crab samples were collected by net hauling from the three locations (Site A: sewage outfall area; Site B: port area and Site C: contrast area). For comparison, seven kinds of mollusks from the aquaculture in the bay were purchased from the local seafood markets of Yantai.

Each kind of marine organism contained at least 30 individuals. All samples were placed for approximately 24 h in filtered seawater. This allowed them to empty their gut, without eliminating hydrophobic contaminants. The samples were placed in polyethylene bags and frozen at −20°C until chemical analysis. Prior to extraction, shucked mollusk samples were homogenized and freeze-dried. Subsamples were dried to constant weight to determine the water contents, and eventually were ground into fine powder. The shrimp and crab samples were homogenized with their whole bodies.

The pretreatment was conducted according to the method by Tanabe et al. (2000). Approximately 10 g well homogenized soft tissues were mixed with anhydrous Na_2SO_4, until the homogenate was free-flowing. The mixtures were extracted using 80 mL hexane–dichloromethane mixture (1:1 v/v) with sonication method for 60 min, and then stood overnight. Decachlorobiphenyl (PCB 209), $^{13}C_{12}$-PCB 47 and $^{13}C_{12}$-PCB183 were added as surrogates prior to the extraction. The extract was concentrated on a rotary evaporator to about 1 mL. The concentrated extract was further purified by elution through a glass column (12 mm i.d.) filled with 2 g silica gel and 2 g florisil column. The analyses were eluted using 20 mL n-hexane and 20 mL 3:1 (v/v) n-hexane: dichloromethane in turn. The two fractions were combined and the volume of samples was adjusted to about 1 mL by a gentle stream of nitrogen gas.

The quantification of PBDE was measured using an Agilent 890A gas chromatograph (GC) with a ^{63}Ni electron capture detector (micro-ECD) (Agilent, USA). A HP-1 fused-silica capillary column (60 m × 0.25 mm i.d., 0.25 μm film thickness) was used for the determination of PBDE congeners, except for BDE 209. A VFS column (10 m × 0.25 mm i.d., 0.25 μm film thickness) was used for BDE 209 analysis. High purity N_2 was the carrier gas and make-up gas at flow rate of 1 and 49 mL/min. 1 mL of the extracts was injected into the injector at 250°C with programmable temperature vaporization (PTV). The oven temperature was raised from 80 to 200°C at a rate of 10°C/min, hold for 1 min, and then programmed to 270°C at 5°C/min, hold for 5 min. The injector and detector were maintained at 250 and 280°C, respectively. GC peaks were identified with the accurate assignment of retention times of PBDEs standards (the National Research Center for Certified Reference Materials of China), and further confirmed by an Agilent 6890 N GC–MS system. The residues of PBDE 28, 35, 47, 99, 100, 138, 153, 154, 183 and 209 were quantitatively determined by the calibration curves of the standards using peak areas. The quantitative determinations were performed by internal standard procedure.

One procedural blank and one spiked blank consisting of all chemicals were run with every batch of 10 samples to assess potential sample contamination. Only small concentrations of BDE 47 were found in procedural blanks and they were appropriately subtracted from those in the sample extracts. Three duplicate samples reported RSDs within 20 % for all the target chemicals. The average recoveries of surrogate standards (PCB 209, ^{13}C-PCB 47 and ^{13}C-PCB 183) varied from 84.4 % to 111 %. Reported values were not corrected by surrogate recovery. The detection limit was 0.01 ng/g for PBDEs.

Results and Discussion

The contents of ten PBDE congeners identified in mollusks collected from the local seafood market of Yantai coast are shown in Fig. 2. Among the samples analyzed in this study, detection frequency of $\sum$PBDEs was 100 %. These results indicated ubiquitous contamination of $\sum$PBDEs in the Yantai coastal environment. The concentration range of $\sum$PBDEs was 0.23–10.56 ng/g, with a median value of 3.52 ng/g. The concentrations of PBDEs were all below the national standards 40 ng/g d.w. for seafood. The total concentrations of PBDEs in *Myt* were the highest among all mollusks. On the contrary, *Sax* accumulated the lowest PBDEs. Among the 10 PBDEs measured in this study, the abundant PBDE 28, 47, 99, 100, 154, 209 in mollusks were found in this report. BDE 47 and BDE 209 were the predominant congeners, accounted for 28.7 % and 48.7 % of

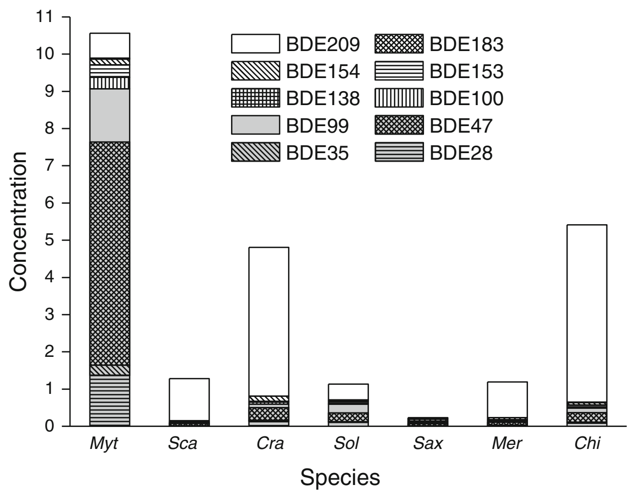

Fig. 2 PBEDs concentrations in mollusks (*Mytilus edulis*, *Scapharca subcrenata*, *Crassostrea*, *Sol sricus*, *Saxidomrs purpuratus*, *Meretrix meretrix* and *Chiamys farrer*) collected from seafood market of Yantai Sishili Bay, China (Unit: ng/g d.w.)

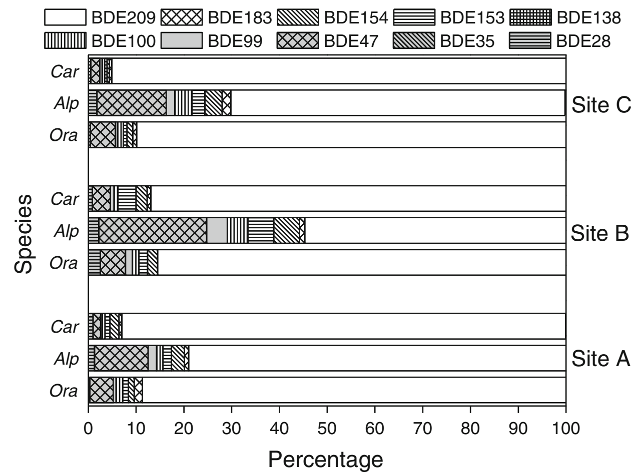

Fig. 3 Percentage of individual BDE congeners to total PBDE concentrations in the shrimps (*Oratosquilla oratoria* and *Alpheus distinguendus*) and the crab (*Carcinoplax vestitus*) collected from sampling sites along Yantai Sishili Bay, China (Unit: %)

total PBDEs while BDE 183 was much lower and BDE 138 were not found in all mollusks. BDE 209 dominated the PBDE profile for certain species – *Sca*, *Cra*, *Mer* and *Chi*, whereas BDE 47 dominated the PBDE profile for certain species – *Myt* and *Sax*. This is consistent with the fact that BDE 47 is one of the most bioaccumulative congeners from the commercial Penta-BDE mixture (Oros et al. 2005). de Boer et al. (2000) reported that mussels in the Rhine River can selectively accumulate PBDE 47, which is the restricted penta-Cl congener in EU countries, has been found in air, food, and human tissues and received widespread concerns (Yang et al. 2004). Jones et al. (2001) suggested that the persistent existence of PBDE 47 in the environment should be an evidence of historically remaining large sources or recycling processes gradually releasing into the environment. The high concentrations of BDE 47 suggested the past use of PBDEs in this area. One reason for the high percentage of BDE 209 was that a large quantity of BDE 209 was used in Asia/China as well as its high concentrations in some of the sediments from the Pearl River Delta (Mai et al. 2002).

PBDEs concentrations in the shrimps and crabs which were collected from three sites by net hauling were consistently analyzed and the percentage of individual congeners to total PBDE concentrations is illustrated in Fig. 3. On the whole, concentrations of pentabrominated diphenyl ether congeners (BDE 35 and BDE 138) were below the detection limit in all samples in the studied zones, whereas other congeners were above the detection limit in all samples. PBDEs concentrations varied in individual species and in sampling sites. The median concentration of ∑PBDEs in *Ora*, *Alp* and *Car* from three sites was 2.92, 1.42 and 2.18 ng/g, respectively. In the shrimps and crabs samples investigated, the total level of the PBDE congeners were dominated by BDE 209 (>70 %), except for samples of *Alp* in Site B. This contrasted with the above observations of the mollusks. One possible reason for this is that the mussels are suspended in the water column and have less access to sediments while shrimp and crabs are more associated with sediments and more likely to encounter enriched PBDE concentrations. As far as the sampling locations were concerned, the concentration range of ∑PBDEs in the samples collected from Site A (the sewage outfall area), Site B (the port area) and Site C (the contrast area) was 2.24–3.45, 0.93–2.83 and 1.1–2.47 ng/g, respectively. There is a distinct trend of decreasing concentrations of PBDEs from site A to B to C, which suggests that the specimens collected from the sewage outfall area are potentially enriched in the more highly brominated congeners relative to those from the other two collections sites. This re-affirms that sewage outfalls reflect a likely source of PBDEs to the environment.

To assess the current situation of POPs contamination in marine organisms from Yantai coastal area, we compared the published data for ∑PBDEs residues in *Cra.* from various regions and times (Table 1). We found the PBDEs contents varied markedly. In general, contents in the *Cra.* of the Yantai coastal area were not very high and the contamination was moderate.

Comparing PBDE concentrations in this study with those in bivalves from other Asian countries (China, Hong Kong, Japan, Philippines, Vietnam, Korea and India) (Ramu et al. 2007) and European countries (France, Greenland, UK) (Christensen et al. 2002; Johansson et al.

Table 1 Comparison of ∑PBDEs concentrations in mollusks between this study and published data (Unit: ng/g d.w.)

Years	Location	∑PBDEs[a]	Reference
2009	Yellow Sea, China	0.23–10.56	Present study
2000	Greenland	0.5[b]	Christensen et al. (2002)
2002	USA	nd−50[b]	Oros et al. (2005)
2001	French	0.5–10[b]	Johansson et al. (2006)
2004	Japan	0.15–4.65[b]	Ramu et al. (2007)
2004	China	0.15–1[b]	
2004	Hong Kong	0.5–10[b]	
2004	Philippines	1–5[b]	
2004	Vietnam	0.01–0.3[b]	
2004	India	0.05–0.2[b]	
2004	Korea	0.15–4.5[b]	
2006	UK	1–15[b]	Fernandes et al. (2008)

[a] Sum of tri- to hepta-BDEs

[b] Data on wet weight reported in the original paper was converted into dry weight assuming moisture content as 80 %

2006; Fernandes et al. 2008) and North America country (USA) (Oros et al. 2005), it was found that PBDE levels in mussel tissues from coastal waters of Asia were comparable or higher than those reported for mussel tissues from Europe but lower than mussels from the USA. The mussels in USA were the highest, which was about 5 times higher than our data. The lower concentrations of PBDEs in India, Vietnam, and Greenland potentially reflect the voluntary phasing out of these compounds, and those in other countries might also indicated smaller usage and/or earlier regulation of PBDEs. These results were co-incident with findings of other studies summarized by Hites (2004), that the environment and people from North America are more contaminated with PBDEs as compared to other regions. The ∑PBDEs concentrations in our report were higher than those reported in a previous mussel watch study in China in 2004 (Ramu et al. 2007), which may suggested different sources of PBDEs input to the waters.

Generally, the bivalve, shrimp and crab samples collected from Sishili Bay have been contaminated by PBDEs. The levels of PBDEs in the mollusks purchased from the seafood market of Yantai varied greatly, depending on the PBDE congeners and organism species. While the PBDEs contents in shrimp and crab samples collected from three areas varied in individual species and in sampling sites. However, the concentration level in these samples was not exceeding the edible criteria. To some extent, probable health associated problems might be encountered in people consuming excessive shrimps, crabs and mollusks and more emphasis should be placed on continuous monitoring of these compounds.

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